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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: CLEANING METHOD

(57) Abstract: This invention relates to a method of softening water and/or in which the deposition of hard water scale is inhibited. The invention relates in particular to such a method carried out in a domestic environment. The invention also relates to compressed water-softening compositions for such methods in which 50% or greater of the particles of citric acid or a salt thereof are greater than 200 microns and 10% or less of the particles of citric acid or a salt thereof have a particle size of more than 200 microns.



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CLEANING METHOD

This invention relates to a method of softening water and/or in which the deposition of hard water scale is inhibited. The invention relates in particular to such a method carried out in a domestic environment. The invention also relates to compressed water-softening compositions for such methods in which 50% or more of the particles of citric acid or a salt thereof are greater than 200 microns and 10% or less of the particles of citric acid or a salt thereof are less than 200 microns.

It is well known that certain metal compounds, notably calcium compounds, when present in water, have a significant effect on the properties of the water. For example, "hard" water containing a significant loading of soluble calcium and magnesium compounds may require a large amount of soap or detergent in order to form a lather. Scale deposits can readily form from such water, for example on heating or pH change or evaporation. These can be encrustations, or watermarks left on evaporation of water droplets from, especially, a shiny surface.

There have been many proposals for removal of metal ions from aqueous solutions. In the industrial context proposals have included filter beds and polymeric filters for capturing heavy metal ions from an aqueous solution flowing within a passageway. Examples are given in EP992238A and GB20869564A. In the domestic context chelating compositions can be added to an aqueous washing solution and these can capture metal ions, such as

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calcium ions. Examples of chelating compositions are given in EP892040A.

Increasingly popular is the delivery of cleaning and water-softening compositions as compressed compositions, typically a tablet. These are convenient providing a unit dosage which is easily handled. Difficulties arise in the production of such compressed compositions in balancing the needs that the compressed composition is suitably hard and non-friable under transportation conditions but yet is not so compacted that it cannot easily disintegrate. Suitable levels of "hardness" are between 150 N and 250 N (the test conditions being set out in the Example section). Suitable levels of "friability" are between 2% and 9% (the test conditions being set out in the Example section). Suitable "disintegration" times are between 5 seconds and 180 seconds, when placed in 1 l of gently stirred water.

Multi-region compressed compositions are now of interest in being able to provide such advantages as differential release of actives, or delayed release of one region. Developing multi-region compressed compositions is time consuming and expensive due to ingredients reacting to the same physical conditions in different ways, such as moisture or temperature fluctuations. This may lead to problems at the interface between the regions and the need to prevent separation, which can be caused, for example, by differential expansion. Therefore there is a need to balance the physical properties between the regions even where the composition in each region may be different. To

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aid ease of development the starting point is usually to start by keeping the compositions between the regions as similar as possible.

5 A particular problem found with producing such a multi-region product is that the water-softening ingredients are generally highly crystalline and are not easily produced into compressed formulations, such as the citrate and silicates.

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 We have found that for certain common actives in water-softening compositions the distribution of the granulometry of citric acid, or a salt thereof, is important in the manufacture of compressed compositions,
15 in particular water-softening compositions which contain a high proportion of this ingredient. The selected particle size distribution improve binding properties. The resulting compressed composition is in fact more stable and maintains acceptable levels of friability and
20 of disintegration for a longer time. Also the aesthetic of the compressed composition is better.

 Therefore we present as a feature of the invention a compressed composition comprising citric acid, or a salt
25 thereof, in which 45%, or greater than 45%, or greater than 60%, ideally greater than 90%, or at least 95% of the particles have a size of at least 200 microns, 300 microns or 400 microns. Preferably 60%, or greater than 45%, of the particles have a size greater than 425
30 microns or of 425 microns or more. Preferably 10% or less of the particles of citric acid or a salt thereof have a particle size of less than 200 microns.

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An alternative feature of the invention is the use of citric acid, or a salt thereof, in which 60%, preferably greater than 60%, of the particles have a size of at least 425 microns in preparing a compressed water-softening product.

Additional water-softening actives may also be present as described below. A preferred active is a homo or co polymer of the following monomeric units or a salt thereof; an acrylic acid, a maleic acid, a sulfonic acid or a phosphonic acid.

We have also found that the distribution of citric acid, or its salt, between the regions of the compressed formulation affects the values discussed above. A preferred distribution is the weight excess of citric acid or its salt in at least one region is at least 5%, ideally greater than 7%, 10%, 12%, 20%, 50%, 75% or 95% greater than in a second region.

There are three main types of method of action for water softening actives, described below.

1) Ion exchange agents - such agents include alkali metal (preferably sodium) aluminosilicates either crystalline, amorphous or a mixture of the two. Such aluminosilicates generally have a calcium ion exchange capacity of at least 50 mg CaO per gram of aluminosilicate, comply with a general formula:



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and incorporate some water. Preferred sodium aluminosilicates within the above formula contain 1.5-3.0 SiO₂ units. Both amorphous and crystalline aluminosilicates can be prepared by reaction between sodium silicate and sodium aluminate, as amply described in the literature.

Suitable crystalline sodium aluminosilicate ion-exchange detergency builders are described, for example, in GB 1429143 (Procter & Gamble). The preferred sodium aluminosilicates of this type are the well known commercially available zeolites A and X, and mixtures thereof. Also of interest is zeolite P described in EP 384070 (Unilever).

Another class of compounds are the layered sodium silicate builders, such as are disclosed in US-A-4464839 and US-A-4820439 and also referred to in EP-A-551375.

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These materials are defined in US-A-4820439 as being crystalline layered, sodium silicate of the general formula

25
$$\text{NaMSi}_x\text{O}_{2x+1} \cdot \text{yH}_2\text{O}$$

where

M denotes sodium or hydrogen,
30 x is from 1.9 to 4 and y is from 0 to 20.

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Quoted literature references describing the preparation of such materials include Glastechn. Ber. 37,194-200 (1964), Zeitschrift für Kristallogr. 129, 396-404 (1969), Bull. Soc. Franc. Min. Crist., 95, 371-382 (1972) and Amer. Mineral, 62, 763-771 (1977). These materials also function to remove calcium and magnesium ions from water, also covered are salts of zinc which have also been shown to be effective water softening agents.

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2) Ion capture agents - agents which prevent metal ions from forming insoluble salts or reacting with surfactants, such as polyphosphate, monomeric polycarbonates, such as citric acid or salts thereof, EDTA, algins, alginates.

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3) Anti-nucleating agents - agents which prevent seed crystal growth, such as polycarbonate polymers, such as polyacrylates, acrylic/maleic copolymers, and acrylic phosphonates and sulfonates.

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The compositions may be used in ware washing using a machine or a manual method. The compositions may also be used to soften water in other cleaning methods such as hard surfaces, for example using a hand-cloth or mop, and an open vessel, for example a bucket or bowl. Thus, the cleaning method could be a method of cleaning a hard surface, for example a window, a tiled surface, shower screen, dirty tableware and kitchenware, a sanitary article, for example a bath, shower screen, lavatory, wash basin or sink, a car or a kitchen worktop.

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The invention will now be described, by way of embodiment, with reference to the following examples.

Hardness Test

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Using a dynamometer with a test piston diameter of 8 mm and a piston speed 30 mm per minute (a machine such as the ERWEKA tablet hardness tester THB 30 may be used) the maximum hardness of the tablet just prior to breakage is recorded for 4 tablets in the same orientation and averaged.

10

Friability Test

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Ten tablets are weighed and placed into a square plastic sample holder of approximate dimensions 110×110mm square by 170mm long. The sample holder is rotated horizontally along its length at 50 rpm for 1 minute. The tablets are weighed again and the amount of material loss expressed as percentage

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$$\% \text{ friability index} = \frac{W_0 - W_1}{W_0} \times 100$$

where:

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W_0 = initial weight

W_1 = weight of the tablets after one minute of test at 50 rpm

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Sodium citrate was used of the following granulometry

PRODUCT	1000 μ	850 μ	600 μ	425 μ	212 μ	125 μ	63 μ	<63 μ
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COARSE	0,08	3,58	39,3	33,46	17,4	4,60	1,38	0,17
COARSE1	0,51	1,67	20,71	32,56	33,24	8,70	2,29	0,29
COARSE2	1,55	3,62	21,88	21,41	42,86	7,45	1,17	0,06
FINE	0	0,06	1,27	22,12	64,26	9,54	2,4	0,35

Below is an example of formula in which the use of the above citrate is used.

Raw Materials	Region1	Region2
Polymer	28	28
Citrate	57.8	54.69
Binder/ Disintegrant	14.2	15.29
Silicate		2
Dye		0.016
TOTAL	100	100

CLAIMS

1. A compressed composition comprising citric acid, or a
5 salt thereof, in which greater than 45% of the particles
have a size of at least 425 microns.
2. A compressed composition comprising citric acid, or a
salt thereof, as claimed in claim 1, in which greater
10 than 60% of the particles have a size of greater than 425
microns.
3. A compressed composition comprising citric acid, or a
salt thereof, as claimed in claim 1, in which greater
15 than 95% of the particles have a size of at least 200
microns.
4. A compressed composition comprising citric acid, or a
salt thereof, as claimed in any claim from 1 to 4, in
20 which the percentage of particles as defined have a size
of at least 300 microns.
5. A compressed composition comprising citric acid, or a
salt thereof, as claimed in any claim from 1 to 4, in
25 which the percentage of particles as defined have a size
of at least 400 microns.
6. Use of citric acid, or a salt thereof, in which
greater than 60% of the particles have a size of at least
30 425 microns in preparing a compressed water-softening
product.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C02F5/10 C11D17/00 C11D3/20

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C02F C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 99 02640 A (BUSCH ALFRED ;HERBOTS IVAN MAURICE ALFONS JA (BE); PROCTER & GAMBL) 21 January 1999 (1999-01-21) page 65, line 10-13; examples 14,21 -----	1-6



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
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INTERNATIONAL SEARCH REPORT

Information on patent family members

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Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 9902640	A	21-01-1999	WO 9902640 A1	21-01-1999
			AU 3668297 A	08-02-1999
			BR 9714811 A	03-10-2000
			EP 1002041 A1	24-05-2000
			JP 2001509539 T	24-07-2001
